2020

HHpXRF study of recent zinc and lead pollution on lava stepping stones from Pompeii: Tourist footfall, tyre dust and leaded petrol

Michael Worthing

Lloyd Bosworth

M. Papandrea

Eric E. Poehler

Steven Ellis

See next page for additional authors

Authors
Michael Worthing, Lloyd Bosworth, M. Papandrea, Eric E. Poehler, Steven Ellis, and Ray Laurence

archaeometry

Archaeometry ••, •• (2020) ••–•• doi: 10.1111/arcm.12570

HHPXRF STUDY OF RECENT ZINC AND LEAD POLLUTION ON LAVA STEPPING STONES FROM POMPEII: TOURIST FOOTFALL, TYRE DUST AND LEADED PETROL*

M. WORTHING and L. BOSWORTH

Department of Classical and Archaeological Studies, University of Kent, Canterbury, CT2 7NR, UK

M. PAPANDREA

3 Hemlock St., Paxton, MA 01612, USA

E. POEHLER

Classics Department, University of Massachusetts, Amhurst, MA 01002, USA

S. ELLIS

Department of Classics, University of Cincinnati, 410 Blegen Library, PO Box 210226, Cincinnati, OH, USA

R. LAURENCE†

Department of Ancient History, Macquarie University, Sydney, NSW 2109, Australia

A helium-enabled Niton X-ray analyser (HHpXRF) study of 296 lava stepping stones from ancient Pompeii showed that their surfaces were contaminated with superficial deposits of Zn and Pb. Recent research has shown that concentrations of these elements are highest in urban areas, where they were attributed to tyre dust and leaded petrol, respectively. The distribution of these elements on the stepping stones is represented on maps of the site. Zn pollution is most abundant in areas visited by tourists and is attributed mostly to wear from their rubber-soled footwear. Pb pollution is attributed to the movement of onsite vehicles using leaded petrol.

KEYWORDS: POMPEII, STEPPING STONES, HHPXRF, GEOCHEMISTRY, ZINC AND LEAD POLLUTION, TOURIST FOOTFALL, LEADED PETROL

INTRODUCTION

The ancient Roman port city of Pompeii was founded in the sixth or seventh centuries BCE and became a Roman colony in 80 BCE. In 79 CE it was destroyed by a catastrophic eruption of Mount Vesuvius, which buried the city under several metres of ash and pumice (Pliny the Younger *Letters*, 6. 16 and 6.20; Sigurdsson *et al*. 1982). After the eruption, the site was lost for some 1500 years, until it was rediscovered in 1599. In 1748, the Spanish engineer Rocque de Alcubiere re-examined the site and this and subsequent excavations have revealed a detailed snapshot of Roman life in the first century CE. At the time of its destruction, the city had a forum,

*Received 16 July 2019; accepted 14 April 2020
†Corresponding author: email ray.laurence@mq.edu.au
Peer Review The peer review history for this article is available at https://publons.com/publon/10.10.1111/arcm.12570

baths and temples, an organized system of paved roads, a complex water and sewage system, a gymnasium and an amphitheatre. Its population was about 11,000 people. At present, about two-thirds of the site has been excavated, and it has become one of the most popular tourist destinations in Italy, receiving approximately 2.5 million visitors annually. It was declared a UNESCO World Heritage Site in 1997 (Cicchella *et al*. 2014).

The present paper is based on geochemical data collected from lava stepping stones in the city and drill core material taken from a borehole in the lava flow underlying the city. The borehole was drilled within the city (Di Maio, pers. comm.), but we could not determine its exact location. However, information on each of the seven studied core sections indicated that the site is at 'CANT XII, INS IX'. Data were collected with a hand-held helium-enabled Niton X-ray analyser (HHpXRF) supplemented with an inductively coupled mass spectrometry (ICP-MS) analysis of one of the drill core sections. The initial purpose of the project was to determine the geochemistry of the stepping stones with a view to establishing their provenance. However, anomalies in the data set also suggested that the surfaces of the stepping stones were contaminated with superficial deposits of Zn and Pb. The drill core material provided a pristine standard against which the level of modern pollution could be assessed. The purpose of this paper is to present these data and to suggest possible sources for the pollution. The conclusions may also have wider applications in drawing attention to similar pollution at other heritage sites that draw large crowds, and in urban environments with a high human population and traffic density.

MATERIALS AND METHODS

Stepping stones are a ubiquitous feature of the roads of Pompeii (Poehler 2017a). They are bounded by kerbstones, the majority of which range in height from 15 to 39 cm, resulting in a significant drop from the pavement to the lava-paved road surface (Fig. 1). The resulting canalization of the roads meant they could be used not only for the movement of carts but also as conduits for rain water, wastewater and rubbish. The stepping stones were placed at intervals along the roads and allowed pedestrians to cross the roads without stepping onto the road surface. Thus, they have a similar range in height to the kerbstones. The stones are ovoidal in shape and of more or less standard dimensions, with their long axis arranged parallel to the length of the roads. Poehler (2017a) gives average dimensions as length 124 cm, width 69 cm and height 29 cm. Owing to the fact that they are made almost exclusively from massive lava blocks,this translates into an average of 570 kg. Depending on the width of the roads, either one, two, three or four stepping stones were used at crossing points, which are particularly common at road intersections (Fig. 1). The gaps between the stones were arranged to allow the passage of cartwheels. In terms of conservation, the stepping stones were used both in antiquity and by tourists visiting the site from the time of its excavation. The surface of the stones is flat with little sign of uneven erosion through footfall, in contrast to the rutted surface of the road caused by cart action. There are 316 stepping stones in Pompeii (Poehler 2017a): we collected data from 296 of them.

Mineralogically the stepping stones and the drill core lavas are very similar (Figs. 2, a, b). Di Maio (pers. comm.) also noted that the drill core lavas are typical of lava outcrops around the city. They are strongly porphyritic, consisting of phenocrysts of black prismatic clinopyroxene up to 7 mm in length aligned in a weak flow foliation. Milky equant leucite phenocrysts are also prominent together with rare olivine (Fig. 2, b). Examination of clean rock surfaces with a hand lens shows that the grey-coloured matrix is crowded with sub-microscopic leucite and other minerals (see also Di Renzo *et al*. 2007). Examples of lava outcrops are at Insula I.2.2 (Fig. 2, c) and

Figure 1 *Lava stepping stones in Pompeii along Via Stabiana, which runs uphill from right to left. Note the kerbstones and the resulting canalization of the roads and the slight vesicularization of some of the stones. The gaps between stones allowed the passage of cartwheels, resulting in rutting. Note also the tourists walking across the stones. [Colour figure can be viewed at wileyonlinelibrary.com]*

an unidentified locality within the Insula Meridionalis. The third outcrop is just outside the city to the north-west at Villa dei Misteri (Kastenmeier *et al*. 2010). The lavas are variably vesicular. For example, the outcrop represented in Figure 2 (c) is highly vesicular, whereas the drill cores and stepping stones tend to be more massive though some display minor vesicularity (e.g., Fig. 1). Before the analysis, a small area of each stepping stone was thoroughly cleaned by scrubbing with a plastic brush and clean water. Residues were wiped away with cosmetic wipes. This was followed by further cleaning with 99% ethanol to remove any organic residues and to dry the area before analysis. Discolouration of the discarded wipes indicated that the stones were generally very dirty.

Data were collected with an He-enabled hand-held Niton XL3t 950 He GOLDD+ X-ray portable analyser (HHpXRF), hereafter known as the Niton. This machine has an Au anode (9–50 kV, 0–40 μA max) giving a resolution of $<$ 185 eV. The He attachment permits the determination of lighter elements such as Si, Al, Ca, Mg, P and K, as well as elements between Ti and Bi on the periodic table: Zr, Sr, Rb, Ba, Pb, Fe, Mn, As, Zn, Cu, Ni, Nb, S, Pb, Th, La, Ce, Pr and Nd. Data were collected on 296 stepping stones located throughout the Pompeii site and seven analyses of the drill core lava. Before fieldwork, the Niton was calibrated at the University of Kent, Canterbury, UK, using the method described by Worthing *et al*. (2018). Instrument drift in the field was monitored with a cut piece of a recent cobble stone from Rome (COB1), whose composition had been determined by a full analysis with a laboratory-based XRF machine. In addition, a sample from one drill core was analysed by ICP-MS at the University of Greenwich, London, UK (POMP1).

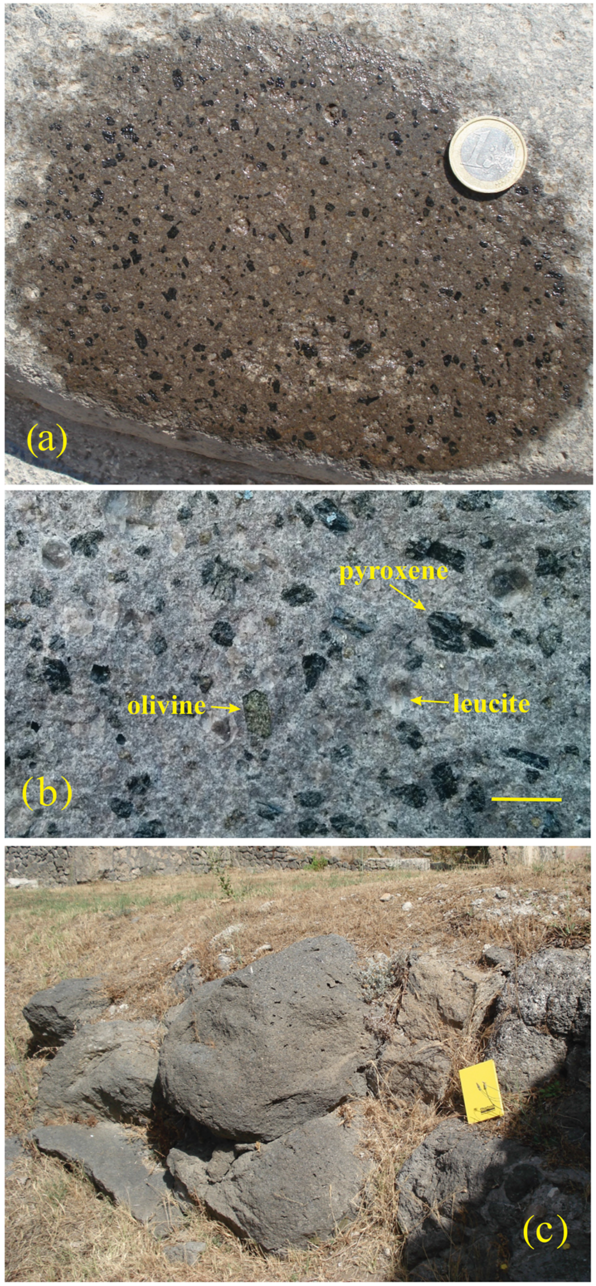

Figure 2 *(a) Lava stepping stone moistened for cleaning. Note the clinopyroxene (black) and leucite phenocrysts (milky). Coin = 23 mm in diameter. (b) Close-up of a broken section of the POMP1 drill core. Note also the clinopyroxene (black), equidimensional leucite phenocrysts (milky) and a euhedral olivine crystal in a fine grained matrix. Bar scale = 7 mm. (c) Lava outcrop at Insula I.2.2. [Colour figure can be viewed at wileyonlinelibrary.com]*

Geochemistry

This section will briefly describe the geological and geochemical context of Pompeii. The earliest phase of magmatic activity of the Somma Vesuvius volcano was dated at 39 to 19 Ka by Di Renzo *et al*. (2007), who also recognized three subsequent phases of activity up to the present day. The first, which occurred between 19 and 10 Ka, was characterized by abundant potassic and ultrapotassic lavas called shoshonites, which now occur as scattered outcrops around the volcano and are generally covered by younger rocks. This description fits the situation of Pompeii as a digital elevation model of the city and its hinterland shows that it was built on a low hill rising above the flat terrain of the Sarno River Basin (Kastenmeier *et al*. 2010). Similarly, geochemical studies (Di Renzo *et al*. 2007; Kastenmeier *et al*. 2010) show that the bedrock of the city comprises shoshonitic lavas that have been assigned to the 19–10 Ka phase of activity.

Kastenmeier *et al*. (2010) attempted to determine the provenance of some of the building materials used at Pompeii. They collected 13 samples from town walls, public buildings, temples, houses and road pavement, and also from the three lava flow outcrops described above (e.g., Fig. 2, c). Unfortunately they did not collect samples from the stepping stones. All samples were subjected to full petrographic and XRF analysis. On the total alkalies silica (TAS) classification diagram, nine of the 13 samples plot in the shoshonite field, including those from the three lava flow outcrops (Kastenmeier *et al*. 2010). POMP1 also plots in the same field. Using the geochemical data, Kastenmeier *et al.* were thus able to suggest a common provenance for the nine construction material samples with the lava flows. In light of the above associations, it is clearly important that a similar provenance be established for the stepping stone lavas. We will address this issue below.

Niton data

Raw Niton data on the stepping stones were collected as element percentage using mining, Cu/Zn mode and a live time of 120 s. The data are presented in Table 1. For processing, the major elements were converted to the geological format of wt% oxide and trace elements to parts per million (ppm). The converted data were loaded into a MinPet 2.02 for analysis. Figures 3 and 4 plot the major and trace element data against SiO_2. They show two important features: first, there is a significant separation between the Niton drill core data and POMP1, as well as the data fields published in Kastenmeier *et al*. (2010); and, second, there is a considerable scatter of the Niton stepping stone data. The reasons for these features will be discussed below.

The geochemistry of igneous rocks is usually determined by crushing and milling rock samples into a fine powder. A weighed portion of this powder is either melted with a flux to produce a glass disc, which is analysed on a laboratory-based XRF, or the powder is digested and analysed by ICP-MS. The grinding up of the whole rock ensures that the analysis represents the bulk rock composition of the sample. However, Niton analysis of *in-situ* rocks such as lava stepping places important limitations on the accuracy of the data. The most important of these limitations relates to the grain size of the lavas and the presence or absence of phenocrysts. The area of the Niton window is about 2 cm^2, which means that only a small part of the rock is irradiated during the analysis. Thus, during routine analysis of phenocryst-poor samples, only matrix analyses are measured and phenocrysts are avoided. This ensures that the analyses are as close as possible to the bulk composition of the rock.

This approach works very well when fine-grained rocks are analysed (Worthing *et al*. 2017, 2018). In these studies, the Niton data compared favourably with the geological XRF data obtained from the abundant geological literature of the Roman volcanic province.

Table 1 *Niton stepping stone, drill core and inductively coupled mass spectrometry (ICP-MS) (POMP1) data.*

Sample	*Major element oxides (wt%)*								*Trace elements (ppm)*					
	SiO_2	TiO_2	Al_2O_3	*FeO*	*MgO*	*CaO*	K_2O	P_2O_5	*Cu*	*Zn*	*Sr*	*Zr*	*Rb*	*Pb*
Drill cores														
core1	45.49	0.92	12.87	9.48	6.57	8.61	4.82	0.45	40	70	820	170	170	20
core2	43.16	0.91	11.63	10.13	5.96	9.31	4.15	0.48	70	70	810	150	150	20
core3	47.48	0.87	15.30	7.05	4.24	7.78	6.29	0.54	90	60	950	150	280	20
core4	47.74	0.97	15.09	6.76	4.59	9.46	5.15	0.56	80	50	990	150	200	20
core5	46.42	0.93	14.11	7.28	4.58	9.09	5.18	0.56	70	50	960	150	210	20
core6	46.97	0.89	14.86	7.08	4.88	7.74	6.27	0.50	50	50	850	120	330	bdl
core7	43.84	0.93	11.43	6.94	4.80	10.49	5.19	0.43	40	60	810	150	220	20
POMP1	52.54	0.90	16.95	6.87	5.75	9.62	5.93	0.64	68	69	776	157	264	23
Stepping stones														
ss001	52.00	0.96	18.54	7.27	5.94	7.73	5.92	0.57	40	190	770	180	310	40
ss002	46.78	0.86	14.16	6.06	4.14	6.21	6.32	0.49	bdl	130	570	140	400	50
ss003	44.78	0.98	13.01	7.16	4.44	7.10	4.86	0.53	50	150	840	190	240	50
ss004	48.08	0.99	11.71	7.45	4.09	8.21	3.85	0.47	80	140	950	190	180	40
ss005	44.30	0.99	13.69	8.68	5.37	8.19	3.43	0.61	60	150	970	190	150	50
ss006	43.29	1.04	12.30	7.96	4.96	9.09	4.07	0.49	50	100	810	200	180	70
ss007	45.46	0.99	14.18	7.93	5.24	8.45	4.30	0.55	50	120	930	190	190	50
ss008	45.64	1.03	14.29	7.51	5.41	7.61	5.06	0.50	50	100	790	170	320	60
ss012	51.75	1.14	20.14	7.47	5.41	7.74	5.06	0.67	60	150	940	190	240	70
ss013	46.52	0.95	13.93	8.80	5.36	7.61	3.51	0.51	70	180	880	160	120	30
ss014	44.38	0.85	13.58	8.11	4.87	6.89	4.81	0.53	70	180	900	170	270	40
ss015	44.83	1.02	12.00	8.31	6.62	11.15	2.95	0.46	60	200	720	160	100	30
ss016	50.19	1.00	17.31	8.19	6.40	9.05	4.49	0.67	50	120	890	180	210	30
ss017	47.50	1.17	15.32	8.62	4.79	8.45	3.84	0.58	60	90	1050	220	140	30
ss018	45.30	0.95	12.68	7.69	4.17	8.31	4.03	0.49	40	150	880	160	180	30
ss019	37.98	0.70	7.82	10.71	6.61	10.34	2.35	0.33	60	120	660	130	200	60
ss019a	42.19	0.82	9.54	7.42	7.61	11.68	2.99	0.36	40	130	750	150	180	50
ss020	50.21	0.94	17.01	7.42	5.15	9.46	4.48	0.53	90	180	1040	150	150	60

(*Continues*)

ss021	44.46	0.93	12.47	7.62	3.61	6.66	3.98	0.51	60	460	1030	190	170	60
ss022	45.76	0.96	13.04	8.95	6.21	10.75	3.05	0.48	60	170	850	160	120	40
ss023	52.45	1.07	19.98	7.02	5.73	8.33	4.76	0.60	60	230	980	200	200	40
ss024	49.71	0.97	17.86	7.27	5.52	8.17	5.25	0.58	60	260	920	210	230	50
ss025	46.78	0.99	13.79	7.51	5.24	10.00	4.41	0.50	60	210	860	190	210	50
ss029	51.57	1.09	17.91	7.78	7.12	7.58	5.62	0.61	90	140	740	150	290	60
ss030	43.88	0.99	11.48	7.79	4.23	7.58	3.85	0.50	70	350	860	180	180	90
ss031	47.71	0.91	15.30	5.60	4.00	5.36	7.78	0.40	80	120	640	150	520	60
ss034	47.66	1.08	16.16	7.69	5.46	9.52	4.17	0.62	40	130	1000	180	200	120
ss035	47.95	1.08	16.05	7.96	4.35	6.35	5.15	0.58	70	180	950	200	230	60
ss036	47.87	0.84	16.02	4.36	3.47	3.73	9.41	0.43	60	150	460	110	610	70
ss037	44.11	0.92	12.25	8.09	4.93	10.11	3.07	0.51	50	140	880	130	120	50
ss038	43.40	0.83	11.55	7.60	4.59	7.28	6.00	0.44	60	100	670	140	350	50
ss039	43.87	0.91	12.38	9.60	4.60	6.98	3.88	0.48	40	330	940	190	180	50
ss042	51.36	0.96	17.82	6.34	5.20	6.84	6.32	0.56	70	80	670	160	380	50
ss043	52.23	1.17	19.73	8.21	6.02	7.28	4.91	0.79	90	130	920	200	220	90
ss044	47.64	0.99	12.98	7.60	4.00	5.14	4.63	0.51	50	530	810	180	240	60
ss063	51.65	1.03	18.46	7.70	4.56	8.70	4.90	0.75	50	200	920	190	190	60
ss070	46.78	0.88	14.13	6.94	3.90	5.52	5.87	0.50	70	80	840	190	310	30
ss084	48.52	0.94	16.04	6.32	4.96	8.01	6.41	0.51	90	200	760	180	360	370
ss085	46.55	1.02	14.68	7.70	5.69	10.37	3.67	0.61	30	190	950	200	140	40
ss086	44.48	0.90	13.23	6.74	4.31	7.37	4.89	0.44	70	200	940	160	220	60
ss087	50.19	1.07	17.15	7.50	5.61	8.31	5.51	0.62	40	100	900	200	250	40
ss088	48.06	1.14	15.37	8.94	6.74	11.08	3.23	0.59	80	100	900	200	130	20
ss093	46.67	0.95	13.79	7.92	4.10	8.60	4.29	0.48	40	160	970	150	170	40
ss094	43.85	0.93	12.20	7.33	3.16	6.80	5.68	0.43	90	170	780	150	340	70
ss095a	45.08	0.93	13.16	7.65	5.62	9.32	4.21	0.52	60	770	760	140	210	30
ss095b	46.22	1.04	14.10	8.46	6.52	10.75	4.24	0.44	60	280	860	140	160	20
ss096	44.59	1.10	11.69	8.24	5.75	12.04	2.57	0.47	50	270	740	180	140	40
ss097	45.63	1.00	13.62	8.59	4.07	6.65	4.76	0.47	80	190	970	200	230	40
ss098	46.09	1.03	13.91	7.36	3.69	7.85	5.35	0.43	60	150	990	210	230	40
ss101	48.55	1.06	16.18	8.16	7.03	11.97	3.65	0.65	40	140	800	180	180	30
ss102	47.85	1.01	15.59	6.43	5.06	7.56	6.42	0.52	60	270	820	190	320	30
ss104	43.77	1.12	11.32	8.45	5.09	10.24	3.15	0.57	60	160	810	180	140	40
ss105	46.90	0.90	14.54	6.91	4.12	6.16	5.46	0.57	40	180	970	170	300	110
ss106	44.46	0.92	13.03	6.53	3.10	5.88	6.66	0.50	50	200	820	170	380	90

(*Continues*)

ss107	44.05	1.10	11.62	7.38	3.89	9.22	4.16	0.53	50	160	780	180	230	80
ss108	46.72	0.92	12.66	9.87	4.91	7.77	6.57	0.62	30	90	1020	190	250	70
ss109	50.41	1.02	17.87	8.95	6.56	6.86	5.05	0.76	50	120	860	200	250	50
ss110	53.19	1.08	20.46	7.64	6.52	9.29	4.90	0.67	50	100	890	190	240	40
ss111	49.50	1.14	16.84	8.23	6.77	10.67	3.60	0.66	60	150	730	170	230	90
ss112	48.31	1.07	16.64	7.71	5.08	9.57	4.69	0.62	60	130	890	160	230	50
ss113	42.98	1.06	12.69	8.84	4.26	6.47	3.78	0.56	40	320	950	200	160	50
ss114	48.15	0.97	17.04	8.21	4.58	7.28	4.55	0.57	50	110	1080	170	200	40
ss115	47.88	0.87	15.64	6.09	4.21	6.02	6.95	0.50	50	150	830	150	370	40
ss116	44.86	1.02	12.33	8.58	4.90	9.80	3.74	0.46	40	120	840	190	180	30
ss117	46.43	1.09	14.23	7.46	3.94	7.95	4.56	0.51	80	120	980	180	230	30
ss118	44.76	0.94	12.93	6.52	3.04	5.46	6.95	0.39	40	130	840	170	380	50
ss119	48.44	1.10	16.57	8.19	5.33	9.74	4.11	0.60	80	90	1000	190	200	30
ss120	46.27	0.96	13.59	7.61	4.70	8.16	5.07	0.51	40	110	920	150	250	130
ss121	49.40	1.02	16.00	8.17	5.65	9.37	4.08	0.66	50	170	930	190	130	50
ss122	50.23	1.01	14.38	8.88	5.18	9.46	2.85	0.64	100	320	1010	190	190	110
ss123	46.55	1.06	14.49	8.81	5.16	8.44	4.19	0.63	20	90	880	170	190	50
ss124	48.74	1.15	16.65	9.23	5.04	7.50	3.92	0.65	60	110	1020	200	150	80
ss125	44.21	0.98	13.81	7.51	3.97	7.72	3.96	0.59	60	150	1060	140	230	120
ss126	46.40	1.12	13.90	7.52	4.98	9.38	5.32	0.53	60	120	790	180	260	80
ss127	46.70	1.22	14.89	7.73	4.14	8.32	4.94	0.53	50	130	960	200	240	70
ss128	47.89	0.92	15.43	5.41	3.60	7.04	7.02	0.41	50	110	700	130	410	120
ss129	47.86	1.03	14.98	6.23	4.07	7.35	6.38	0.47	50	120	700	160	360	60
ss130	45.14	0.96	12.93	5.77	3.71	7.02	5.82	0.49	50	110	760	160	340	90
ss131	47.80	1.06	13.71	7.32	5.88	9.82	3.67	0.52	50	380	920	190	160	240
ss132	45.59	1.12	14.31	9.28	4.71	6.62	3.83	0.61	120	220	960	190	180	130
ss133	42.73	0.95	11.20	6.43	3.33	6.74	5.08	0.48	70	230	800	180	280	310
ss134	47.35	0.97	16.46	8.19	6.33	8.02	6.16	0.58	30	160	850	180	320	50
ss135	50.36	0.99	17.82	7.87	7.79	9.56	4.05	0.62	80	150	1020	180	190	50
ss136	47.40	0.93	15.86	9.00	6.53	7.22	5.11	0.64	70	350	780	170	290	50
ss137	49.71	0.94	17.09	6.01	5.15	7.39	6.27	0.53	40	90	770	160	350	20
ss138	48.31	1.01	16.95	6.73	5.20	7.70	5.32	0.56	60	160	910	190	260	60
ss139	45.17	0.88	13.97	6.49	4.01	5.79	6.24	0.52	40	140	730	150	410	70
ss140	48.42	0.95	18.57	8.09	5.32	8.29	3.32	0.69	100	130	1250	170	130	120
ss141	47.87	1.11	16.21	7.77	4.61	7.68	4.75	0.65	50	110	980	200	220	120
ss142	50.38	0.94	16.92	6.18	4.31	6.49	7.47	0.49	80	130	740	160	410	80

(*Continues*)

ss143	48.08	1.15	16.99	8.35	4.49	8.63	4.28	0.62	60	130	1040	200	160	70
ss144	43.92	0.97	14.02	7.03	4.16	7.29	6.27	0.44	30	140	760	190	320	80
ss145	45.69	1.06	13.00	7.41	5.57	11.02	3.37	0.54	60	130	770	170	170	60
ss146	43.94	0.94	12.04	7.22	4.93	10.02	4.48	0.43	30	130	660	130	310	70
ss147	44.27	0.95	12.72	8.43	3.93	7.95	3.73	0.82	30	120	950	190	130	30
ss148	45.86	1.18	12.81	7.71	5.81	11.47	3.49	0.47	40	130	730	180	190	50
ss149	46.76	1.08	13.89	7.98	6.26	10.81	3.43	0.47	40	120	770	180	170	60
ss150	50.92	1.01	17.70	6.77	6.67	8.96	5.52	0.62	50	140	720	170	270	60
ss151	48.53	1.00	16.95	7.89	5.36	8.60	3.45	0.70	60	150	1090	190	130	80
ss152	47.75	1.00	15.46	7.84	5.87	8.87	3.97	0.63	80	130	970	190	160	60
ss153	48.31	0.92	14.51	6.91	4.84	7.83	4.59	0.44	40	250	770	180	310	100
ss154	45.45	1.01	13.30	8.67	5.75	10.02	3.64	0.53	60	190	910	160	130	50
ss155	48.20	1.03	15.88	8.50	5.08	6.87	5.32	0.58	50	120	970	190	270	30
ss156	50.52	1.07	18.07	7.98	6.07	8.01	5.96	0.60	40	70	770	170	320	30
ss157	48.95	1.07	17.38	8.79	5.62	8.33	4.88	0.56	50	90	1020	180	220	30
ss158	49.36	0.92	15.88	5.50	4.61	8.01	6.77	0.49	110	80	660	130	390	40
ss159	46.60	1.14	12.50	8.25	7.11	12.30	3.31	0.47	30	180	630	130	150	40
ss160	49.07	1.10	16.74	7.94	6.29	8.11	3.91	0.65	60	200	920	200	180	60
ss161	48.75	1.04	16.79	9.19	5.85	7.43	3.65	0.67	50	150	1030	190	140	60
ss162	48.67	0.97	15.73	9.65	6.89	9.61	4.04	0.55	70	90	720	160	220	30
ss163	49.48	0.95	16.68	6.74	4.97	8.32	6.32	0.52	30	110	730	130	340	30
ss164	49.84	1.06	17.69	8.32	4.91	8.26	4.75	0.58	70	100	940	170	240	30
ss165	48.43	1.02	16.49	6.42	4.79	6.91	5.28	0.60	50	140	1020	190	210	40
ss166	51.99	1.05	17.46	7.86	5.58	6.62	4.99	0.71	90	190	1020	200	190	50
ss167	47.70	0.93	12.14	7.51	5.09	12.76	2.63	0.42	110	250	820	170	120	110
ss168	49.01	0.96	16.02	6.17	4.70	6.29	6.93	0.52	60	110	710	160	410	70
ss169	45.42	0.71	13.28	4.20	4.22	5.35	7.93	0.38	40	130	510	110	520	60
ss171	51.28	1.07	18.86	7.68	5.10	9.13	4.48	0.65	50	110	950	200	190	60
ss172	46.20	0.83	13.76	7.52	4.64	6.99	6.14	0.47	40	160	720	130	330	40
ss173	51.65	0.93	18.61	7.52	5.64	6.80	5.54	0.67	50	90	890	180	240	40
ss174	50.12	0.98	16.86	7.95	6.04	9.46	4.81	0.62	80	110	810	180	220	40
ss175	46.01	0.93	13.59	7.83	6.05	9.01	3.56	0.64	110	220	1020	180	130	130
ss176	44.64	1.02	11.32	8.05	6.91	14.73	2.73	0.48	90	170	650	170	120	160
ss177	46.08	0.92	13.13	6.83	4.19	8.56	5.31	0.50	60	80	760	170	300	70
ss178	48.06	1.18	14.57	8.32	4.75	9.16	3.23	0.60	130	90	850	200	160	60
ss179	48.70	0.96	16.29	6.22	3.70	7.76	6.18	0.55	60	110	980	150	280	60

(*Continues*)

ss180	52.54	1.03	18.63	8.07	7.20	11.38	3.53	0.71	50	90	850	150	130	50
ss181	51.02	1.12	15.77	8.29	8.26	13.06	3.01	0.61	60	100	720	150	110	30
ss183	48.17	0.98	16.58	7.56	5.30	7.90	5.47	0.68	50	170	870	160	290	70
ss184	49.21	0.94	16.54	8.00	4.67	6.71	4.68	0.67	40	190	940	190	230	50
ss185	47.88	1.02	15.95	7.74	4.24	7.96	3.94	0.74	40	250	1050	200	160	60
ss186	51.07	0.99	18.24	8.38	6.26	7.65	4.94	0.60	100	100	880	200	220	80
ss188	48.67	1.15	15.90	7.67	4.82	7.51	3.44	0.71	30	200	1020	210	110	70
ss189	49.47	0.89	16.48	5.64	5.38	8.82	6.87	0.52	60	130	550	110	490	50
ss190	47.83	1.14	13.40	9.26	9.59	13.90	2.24	0.51	50	100	750	160	100	30
ss191	48.17	0.94	16.80	6.90	4.81	7.69	5.46	0.59	80	110	820	190	350	40
ss192	49.14	0.88	17.24	6.61	4.69	6.09	6.92	0.56	60	100	810	160	370	40
ss193	47.79	1.11	16.40	8.14	6.43	10.15	4.08	0.57	50	130	1010	200	200	30
ss194	48.79	1.14	15.83	8.16	6.59	8.82	3.74	0.61	80	100	930	200	140	40
ss195	50.55	1.04	18.48	7.53	6.24	8.71	4.19	0.66	50	90	1040	170	190	30
ss196	53.82	1.04	20.76	6.40	5.79	8.03	7.07	0.53	60	140	900	190	300	30
ss197	48.69	1.09	17.39	7.37	5.19	8.83	4.77	0.55	60	100	1040	190	190	30
ss198	43.85	0.76	12.59	4.24	2.98	4.74	9.49	0.34	50	160	500	80	670	100
ss199	45.98	1.12	13.91	8.30	5.79	10.89	3.44	0.55	70	170	910	150	120	210
ss201	56.28	1.00	15.30	8.09	4.81	6.29	3.73	0.49	80	130	1000	230	140	50
ss202	50.26	1.09	18.09	8.08	6.81	9.52	5.01	0.65	50	100	840	190	260	90
ss203	51.42	1.03	16.02	8.01	4.97	5.81	4.08	0.52	70	330	930	190	190	40
ss204	47.71	0.99	16.08	7.21	5.57	9.28	5.73	0.50	70	160	900	200	270	60
ss205	46.12	0.93	13.20	6.65	3.88	6.98	6.56	0.39	40	140	660	160	410	40
ss206	47.79	0.89	14.53	6.90	5.71	7.65	4.81	0.50	60	120	820	150	270	30
ss207	48.11	0.87	15.49	6.82	4.74	5.79	6.78	0.50	60	110	730	140	410	20
ss208	47.67	0.95	15.38	7.30	4.55	7.14	5.75	0.57	70	120	840	180	350	40
ss210	46.28	1.05	14.15	7.58	3.44	7.34	5.11	0.60	40	110	970	190	240	90
ss211	51.23	0.94	19.86	8.23	6.60	6.40	7.01	0.67	70	120	800	180	360	80
ss212	47.88	1.02	15.22	9.51	5.88	8.10	5.01	0.52	70	130	730	180	260	60
ss213	47.01	0.99	14.30	6.46	5.25	8.27	6.16	0.52	40	150	800	150	320	80
ss214	46.15	1.11	14.12	7.30	4.24	7.11	4.96	0.60	40	160	870	190	270	120
ss215	48.55	1.06	15.91	6.67	3.68	5.81	6.53	0.59	60	180	810	170	360	120
ss216	47.01	0.95	14.86	5.61	3.53	5.78	7.52	0.56	40	140	690	150	480	150
ss218	54.27	0.90	19.33	6.90	8.68	8.46	5.12	0.57	90	110	990	160	220	50
ss220	47.37	0.89	15.81	7.90	4.34	8.26	6.06	1.58	70	100	920	140	330	30
ss221	45.18	0.93	13.47	7.28	4.47	8.48	4.76	0.58	100	90	930	180	250	150

(Continues)

ss222	51.36	0.80	18.22	5.97	3.76	4.53	9.67	0.49	30	90	640	150	490	40
ss223	49.98	0.94	17.16	7.64	5.11	6.96	6.85	0.62	60	130	820	190	360	170
ss224	47.77	1.17	15.79	8.50	5.04	9.44	3.54	0.63	60	160	1050	190	130	40
ss225	45.97	0.90	13.38	7.75	4.10	7.12	5.43	0.51	70	120	800	190	290	120
ss226	44.77	0.92	13.30	6.72	3.46	7.59	4.94	0.50	60	110	1000	200	220	110
ss227	47.03	1.12	14.35	8.02	5.46	9.41	3.94	0.55	50	140	890	190	180	90
ss228	45.98	0.91	13.07	6.54	3.90	6.70	5.29	0.54	30	150	880	140	270	70
ss229	44.76	0.95	12.11	8.41	4.20	6.42	4.20	0.55	90	190	900	170	160	120
ss230	45.45	1.10	10.94	8.08	8.03	12.75	2.58	0.44	50	150	640	140	120	260
ss231	47.72	1.04	15.73	7.10	4.89	8.83	4.52	0.48	50	110	970	180	230	50
ss232	50.80	1.03	18.99	7.41	5.29	8.05	4.59	0.60	80	190	950	170	200	100
ss233	48.09	0.96	16.25	7.69	4.43	8.24	4.61	0.58	50	160	1080	190	160	50
ss234	49.92	1.01	18.24	8.25	4.74	8.39	3.53	0.75	30	110	1150	190	130	70
ss235	49.47	1.14	16.87	7.46	5.74	8.92	4.27	0.68	40	150	830	170	230	60
ss236	52.40	1.10	18.74	6.43	4.78	7.74	4.83	0.65	50	300	860	170	290	110
ss237	51.80	1.07	19.53	7.80	5.38	8.06	4.86	0.68	40	110	940	190	230	90
ss238	48.28	0.92	16.98	6.72	4.69	7.71	4.95	0.53	40	90	940	170	230	40
ss239	46.90	0.97	15.87	8.17	5.25	8.50	3.95	0.64	40	240	920	190	190	60
ss240	51.65	0.98	18.34	9.56	7.30	10.64	4.20	0.61	50	160	760	190	170	110
ss241	48.37	1.07	15.05	6.68	5.18	9.26	6.01	0.57	50	260	690	160	320	60
ss242	50.16	0.96	16.78	6.81	4.54	7.46	6.60	0.90	40	130	710	190	360	70
ss243	48.81	0.92	16.12	6.18	5.96	8.12	5.31	0.63	80	120	690	150	390	30
ss244	51.68	1.21	19.49	8.59	6.62	9.54	3.72	0.72	50	160	1150	170	160	40
ss245	50.27	0.99	17.91	7.43	6.16	8.31	4.52	0.59	40	220	930	180	200	70
ss246	52.58	1.01	20.91	7.45	5.17	6.94	5.76	0.66	60	110	940	190	270	50
ss247	48.60	1.00	16.85	6.69	5.44	6.71	7.03	0.60	70	170	840	190	370	100
ss248	49.90	1.11	17.46	7.47	5.33	6.88	5.60	0.65	40	130	860	190	280	80
ss249	45.61	1.03	13.99	6.78	4.80	9.71	4.54	0.54	90	160	770	170	240	110
ss250	52.57	1.13	19.14	8.59	7.99	10.12	4.15	0.62	40	100	860	200	170	30
ss251	50.35	0.88	16.17	7.38	5.32	7.21	3.84	0.53	50	210	980	170	170	50
ss252	49.42	0.88	16.42	9.15	5.07	7.23	3.79	0.69	40	140	1000	180	140	80
ss253	47.24	0.97	15.02	7.36	4.73	7.17	4.91	0.54	100	80	900	190	250	30
ss254	45.47	1.03	14.35	7.13	4.16	7.81	5.84	0.52	60	110	880	200	250	30
ss255	48.37	1.04	15.83	7.93	5.36	7.95	4.61	0.53	90	100	910	190	250	30
ss256	50.64	0.96	16.34	8.90	7.51	7.51	3.87	0.54	90	280	820	150	140	40
ss257	46.85	0.80	13.86	6.40	4.15	5.47	6.66	0.51	100	150	660	150	450	30

(Continues)

ss258	51.97	1.00	19.13	7.37	5.66	7.69	5.79	0.61	40	80	970	170	270	30
ss259	49.12	1.08	16.39	8.87	5.47	8.51	3.96	0.59	70	120	1010	230	130	30
ss260	50.78	0.99	17.59	6.81	4.64	7.23	5.94	0.57	40	140	900	180	310	50
ss261	50.88	1.16	17.80	8.07	4.60	7.97	4.51	0.64	50	90	990	210	200	40
ss262	46.05	0.84	13.71	5.50	3.63	6.04	6.24	0.50	30	160	700	160	380	40
ss263a	41.96	0.88	10.16	7.18	3.51	7.84	5.56	0.44	50	130	700	130	280	30
ss263b	49.12	1.01	15.06	8.35	5.68	11.21	3.65	0.50	60	90	810	160	130	30
ss264a	47.07	0.87	14.23	5.51	3.19	5.74	8.29	0.43	60	120	760	120	450	30
ss264b	44.96	0.94	11.65	7.06	3.34	7.68	3.89	0.45	50	170	990	150	140	50
ss265a	49.80	0.91	16.92	7.34	4.06	6.81	7.00	0.54	50	170	830	160	320	140
ss265b	46.19	0.84	13.26	9.86	5.00	6.74	5.24	0.47	40	130	790	150	260	30
ss266	46.07	0.91	13.91	8.79	5.16	8.69	4.45	0.51	30	140	830	160	190	50
ss267	46.47	0.93	13.39	8.98	6.56	8.69	4.42	0.53	70	180	970	150	190	70
ss268	51.90	0.90	17.75	7.10	4.30	5.87	7.06	0.63	40	130	790	190	370	150
ss269	49.91	0.93	17.34	9.38	5.55	7.13	3.59	0.67	50	250	1040	190	130	170
ss27	51.49	0.99	19.46	7.15	4.96	6.80	5.88	0.60	70	100	1020	190	260	40
ss270	56.23	0.90	17.50	7.57	4.77	6.50	4.81	0.54	110	350	760	160	250	230
ss271	43.00	0.94	11.49	7.15	3.84	7.08	3.58	0.50	70	230	1060	190	130	60
ss272	42.73	0.82	8.68	6.20	4.64	12.18	2.42	0.47	40	590	670	150	110	120
ss273	47.58	0.95	15.49	8.32	4.64	6.35	4.24	0.70	120	260	1000	200	200	80
ss274	47.23	0.91	14.87	6.60	4.25	6.32	7.00	0.54	70	100	740	170	390	120
ss275	45.03	1.00	13.57	8.28	4.41	6.55	5.08	0.56	40	140	950	210	150	110
ss276	48.67	1.03	15.78	7.53	4.50	7.90	4.70	0.70	40	110	890	200	210	80
ss277	50.82	0.95	17.21	7.55	6.03	8.61	5.22	0.69	30	240	720	170	300	50
ss278	48.53	0.96	16.51	7.23	4.64	8.02	5.04	0.59	40	130	850	180	300	180
ss279	46.84	1.03	14.85	7.10	3.89	5.99	6.60	0.50	70	100	840	170	340	90
ss28	49.04	1.02	17.35	8.07	4.72	9.04	3.53	0.58	30	100	1100	200	160	30
ss280	46.08	1.02	14.50	6.94	3.43	7.24	4.88	0.55	80	100	1040	180	240	130
ss281	51.66	1.01	18.90	8.28	7.03	9.53	4.26	0.69	60	120	940	190	200	70
ss282	46.41	0.92	14.41	8.16	4.72	7.52	3.94	0.57	50	180	950	170	150	90
ss284	45.82	0.78	13.58	5.71	3.92	5.61	6.43	0.48	20	120	760	160	400	40
ss285	51.50	1.02	18.83	6.00	5.29	5.33	7.48	0.60	60	120	670	160	430	70
ss286	51.64	1.07	20.08	7.45	5.42	6.77	6.16	0.60	30	150	980	190	320	40
ss290	48.01	1.10	15.71	8.92	6.14	8.26	3.70	0.70	30	170	1020	200	150	100
ss291	48.02	1.11	15.32	8.69	6.15	9.52	3.32	0.64	50	170	930	200	140	40
ss292	48.47	1.03	15.14	7.47	5.73	8.60	4.17	0.62	40	220	850	180	200	50

(*Continues*)

ss293	43.37	1.09	12.72	8.88	4.72	8.64	3.71	0.55	100	210	920	190	150	110
ss294	44.87	0.80	12.75	4.55	3.01	5.29	9.76	0.24	50	280	530	90	650	140
ss295	43.54	0.89	11.41	6.23	2.94	6.25	5.86	0.46	50	230	830	130	320	140
ss296	41.92	1.01	10.69	7.26	3.34	7.77	4.03	0.43	70	200	920	170	170	120
ss298	51.68	1.20	19.83	7.44	4.91	6.44	7.19	0.66	30	120	880	210	310	90
ss299	45.74	0.85	13.95	6.87	4.16	5.63	5.32	0.53	240	340	880	140	280	40
ss300	51.40	1.02	15.82	7.70	5.88	7.97	4.16	0.53	70	810	900	170	140	80
ss301	54.08	1.02	21.06	7.91	6.64	8.63	4.34	0.70	70	210	1030	180	170	50
ss302	52.79	1.10	19.69	7.65	5.51	5.83	6.44	0.59	50	120	840	190	290	50
ss303	49.18	0.92	14.95	6.40	5.32	5.74	4.65	0.65	bdl	400	890	200	260	60
ss304	49.86	0.98	14.94	7.84	4.75	6.02	4.29	0.67	60	220	860	190	210	110
ss307	46.70	0.97	12.79	6.26	3.95	5.54	5.26	0.45	80	220	810	140	280	70
ss308	49.56	0.83	13.91	7.18	5.46	10.52	4.73	0.53	80	230	720	160	340	100
ss309	50.32	0.97	17.28	7.12	5.76	6.73	4.83	0.63	50	120	970	200	230	30
ss311	50.01	1.08	14.49	7.95	4.76	6.66	4.00	0.58	40	290	900	210	190	80
ss312	51.11	0.94	13.06	7.95	3.72	5.88	4.30	0.46	70	120	1020	210	180	50
ss316	51.81	0.96	19.73	8.67	5.90	6.07	5.81	0.62	40	160	890	180	270	120
ss317	50.38	0.94	18.07	6.69	5.56	6.79	6.35	0.54	40	150	870	190	310	40
ss32	53.24	0.87	14.52	7.42	5.37	7.54	4.58	0.42	90	200	800	180	260	40
ss33	52.15	0.94	14.09	6.89	6.90	8.70	3.16	0.47	60	4800	930	150	130	50
ss40	45.96	0.93	13.48	7.09	4.23	7.82	4.51	0.51	80	110	990	190	230	60
ss41	45.49	0.96	13.18	7.58	3.68	6.33	4.75	0.54	30	270	870	200	260	50
ss45	47.61	1.03	14.90	6.89	5.43	9.31	5.06	0.51	50	170	860	170	270	50
ss51	47.79	0.91	15.63	6.49	3.88	5.86	8.43	0.47	30	110	810	180	370	30
ss52	50.49	1.07	18.42	7.09	5.03	7.09	6.76	0.59	50	130	890	180	290	30
ss64	44.48	0.94	13.16	7.11	3.26	6.32	5.10	0.57	60	130	850	180	320	90
ss64a	46.40	1.06	14.10	7.94	4.44	8.18	4.58	0.55	50	120	910	190	220	90
ss65	42.24	0.99	10.82	6.20	3.99	8.97	4.22	0.74	30	110	730	160	330	90
ss67	48.79	0.96	17.32	6.38	4.62	7.44	5.75	0.54	80	160	1020	170	280	30
ss68	45.36	1.05	13.91	9.03	4.72	10.96	3.25	0.54	60	110	880	180	140	50
ss69	47.05	1.02	14.80	7.67	4.73	7.87	5.94	0.58	30	140	720	170	360	90
ss71	49.78	0.95	17.21	8.80	6.54	9.06	3.78	0.59	50	100	920	180	160	30
ss72	37.93	0.92	8.63	8.26	2.91	7.84	4.30	0.34	50	140	930	170	210	30
ss73	47.82	1.03	15.25	7.38	4.87	8.65	5.68	0.54	50	100	900	180	240	30
ss74	46.38	0.95	14.61	5.76	3.61	6.71	7.12	0.43	40	110	870	180	330	30
ss75	44.33	1.01	12.86	7.14	3.99	6.88	5.63	0.50	40	120	920	170	280	40

(Continues)

ss76	46.59	0.96	14.15	6.58	3.79	6.24	5.49	0.52	50	190	790	170	320	80
ss77	46.62	1.09	14.16	7.83	5.11	9.59	3.13	0.57	50	130	990	180	140	60
ss78	49.64	1.06	16.88	7.85	5.28	8.17	4.99	0.60	40	130	940	200	220	80
ss79	45.74	0.92	13.72	7.23	3.46	6.82	5.28	0.51	50	150	900	170	280	80
ss80	47.29	1.04	14.73	8.54	7.38	12.38	2.43	0.47	40	110	890	180	90	110
ss81	48.49	1.05	15.38	8.58	5.60	9.17	4.98	0.60	110	100	890	210	170	30
ss82	46.62	0.97	14.64	8.08	4.99	9.10	3.87	0.56	70	130	930	190	200	50
ss83	47.02	0.94	14.71	6.80	3.17	6.80	6.13	0.48	70	100	940	180	310	40
ss89	45.26	0.93	13.29	7.38	3.96	8.30	4.23	0.44	50	130	950	180	190	40
ss90	45.11	0.97	12.65	6.64	3.19	5.75	5.96	0.43	60	160	790	190	320	30
ss91	43.98	1.02	12.82	8.73	4.23	7.91	3.40	0.48	60	310	910	200	200	40
ss92	44.26	0.92	11.50	8.39	4.84	10.04	3.91	0.44	80	170	820	160	150	30
ss93	39.43	0.80	8.57	8.01	4.60	11.71	2.98	0.35	50	160	620	150	160	40
ssa	44.42	1.08	12.73	7.30	3.23	7.44	4.48	0.51	40	180	850	170	310	90
ssb	41.86	0.93	10.45	7.30	2.75	8.04	4.18	0.53	40	110	960	180	200	80
ssc	40.18	0.96	9.67	9.27	2.68	6.60	3.75	0.52	50	260	1000	190	180	100
ssca	44.38	1.09	11.25	8.63	3.66	7.52	3.66	0.55	60	170	950	190	170	90
ssd	41.76	0.92	11.01	9.04	3.37	6.83	4.23	0.55	70	240	940	190	200	120
vab800	45.08	0.88	13.59	6.85	5.24	9.37	4.64	0.56	60	150	960	190	180	50
vab801	47.64	1.03	15.11	6.69	6.21	9.00	6.18	0.48	50	110	740	180	330	30
vab994	50.76	0.86	19.13	5.86	4.17	6.93	6.41	0.52	70	190	1000	170	290	40
vab995	50.19	1.12	17.66	7.38	5.54	8.97	4.54	0.62	40	120	1020	180	220	30
vab996	49.35	0.97	16.80	6.56	5.71	8.40	6.55	0.50	80	80	830	140	340	20
vab997	44.74	1.04	13.72	8.44	3.81	7.17	4.03	0.50	80	120	1110	190	160	40
vab998	45.91	1.07	14.64	8.63	4.19	8.12	3.67	0.50	70	160	1130	200	120	50
vab999	46.41	0.85	13.71	7.54	3.68	5.03	6.92	0.41	70	120	780	190	360	60

Note: Bdl, below the detection limits.

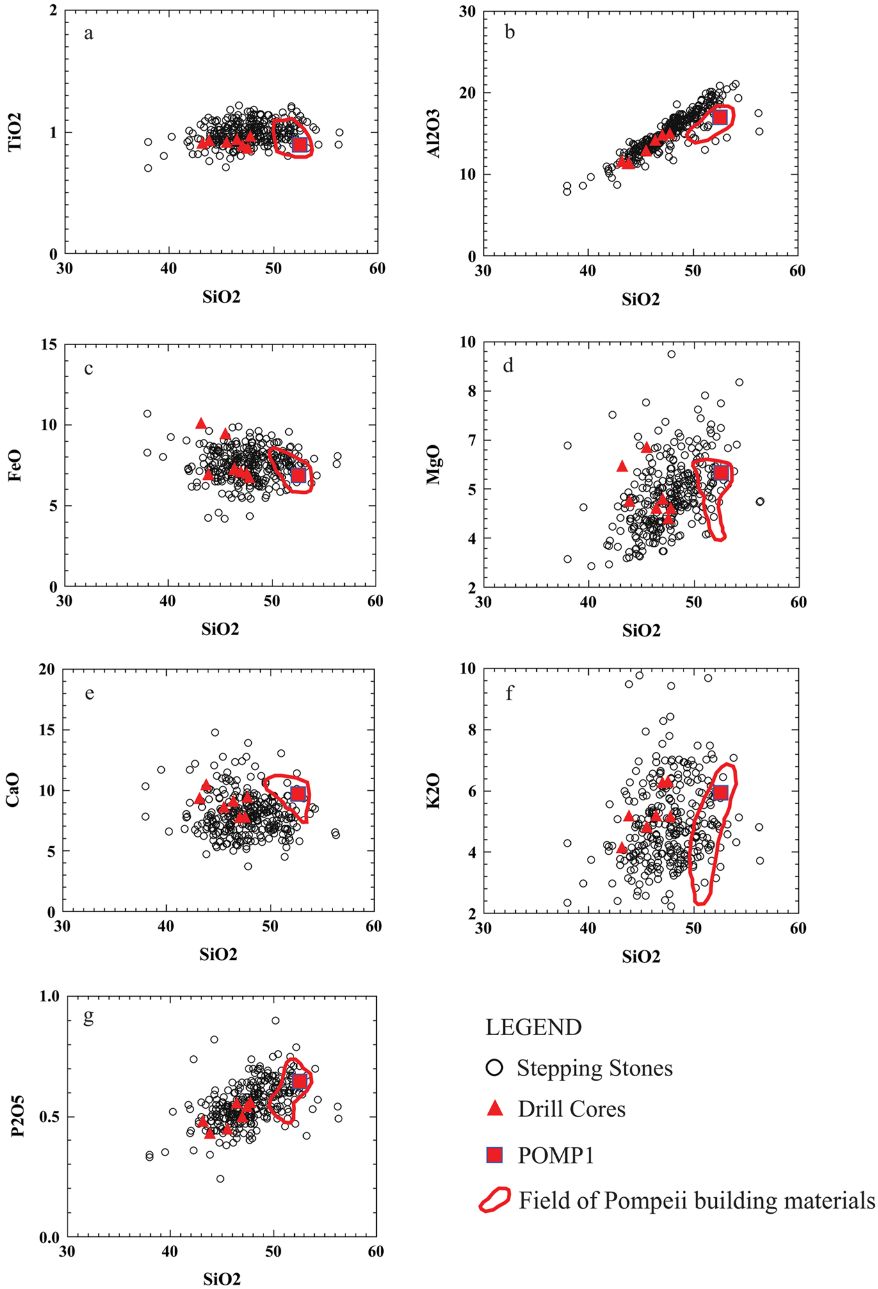

Figure 3 *Selected Niton wt% major element oxides against SiO_2 together with fields containing the analytical data of Kastenmeier et al. (2010). [Colour figure can be viewed at wileyonlinelibrary.com]*

However, it will not work so well with rocks that are relatively coarse grained or have a significant phenocryst content. The analysis of such rocks may mean that some chemical components of the rock may not be included in the analysis, which may therefore be unrepresentative of the

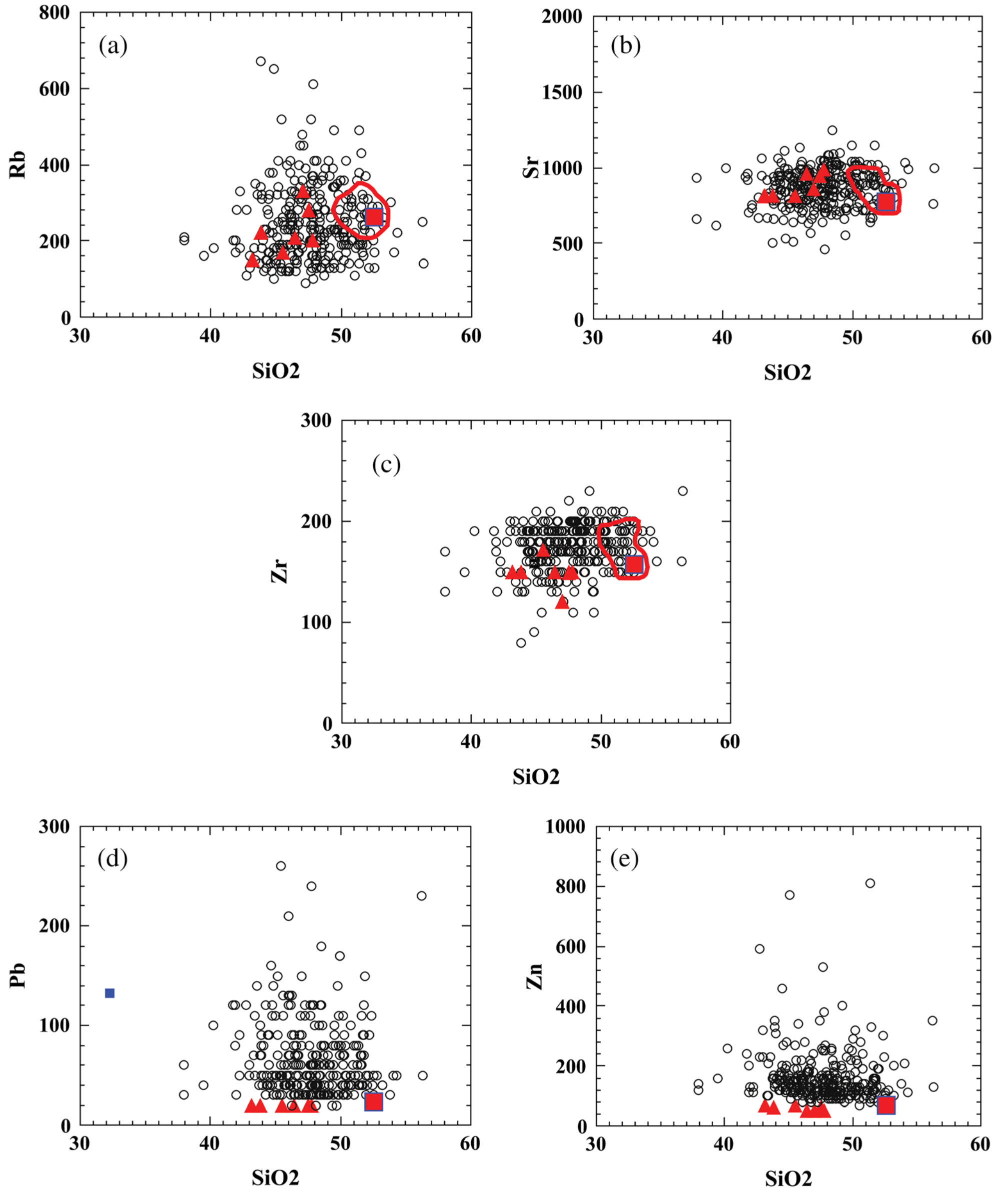

Figure 4 *Selected trace elements (ppm) against SiO_2. For symbols and fields, see Figure 3. [Colour figure can be viewed at wileyonlinelibrary.com]*

bulk composition of the rock. This situation applied in the case of the stepping stones that are the subject of this paper. These lavas are strongly porphyritic and contain crystals of black clinopyroxene $(Ca,Mg,Fe)_2Si_2O_6$) and milky leucite $(K,Na)(AlSi_2O_6)$ (Fig. 2, a, b). The finer grained matrix is also crowded with sub-microscopic leucites and other minerals which may include plagioclase $(Ca,Na,K)(AlSi_2O_8)$, olivine $(MgFe)_2SiO_4$ (Fig. 2, b), and accessory minerals such as magnetite (Fe_3O_4) and apatite $Ca_5(PO_4)_3$ (Di Renzo *et al*. 2007). These minerals will be present in varying amounts in each analysis, which is therefore unlikely to represent the bulk composition of that particular analysis field. We suggest that this effect explains the separation of POMP1 from the Niton drill core data and the scatter shown by the Niton data.

Figures 3 and 4 show plots of selected wt% major element oxides and trace elements against SiO_2. Figures 3 and 4 (a–c) include the fields containing the data of Kastenmeier *et al*. (2010). POMP1 always plots in the same fields as these data. In these diagrams, the drill core data, POMP1 and the fields of Kastenmeier *et al*. (2010) all cluster within the stepping stone field, although the latter tend to plot on the high SiO_2 side. We suggest that this displacement is consistent with the remarks made above about the analysis of porphyritic lavas. We also suggest that these relationships are consistent with a common provenance for the stepping stones, the Niton drill cores, POMP1 and the building materials represented by the data of Kastenmeier *et al*. This implies that the source quarry was either within or close to the city. In support of this, we suggest that the weight of the dressed stepping stones, which averages 570 kg (Poehler 2017a), would have made their transport over large distances problematic. Indeed, Poehler (2017a) states that this weight is greater than the maximum vehicle load set by the Theodosian code. In our view, this further supports the contention that the stepping stones were quarried from a source close to or even within the city. Russel (2013), for example, mentions the existence of a quarry on the western side of the city.

Evidence for pollution

Figure 4 (d, e) plots Zn and Pb against SiO_2 for the stepping stones, the drill cores and POMP1. Unfortunately, the data set of Kastenmeier *et al*. (2010) did not include Zn and Pb, so their fields are absent. The drill core material would have been isolated from the atmosphere before drilling and would thus reflect the pristine Zn and Pb signatures of the rock. Thus, the Zn and Pb values for the stepping stones were calculated by subtracting the concentration of these elements in POMP1 (69.4 ppm for Zn and 22.6 ppm for Pb) from all raw Niton stepping stone data. Subtraction of this primary geological signature means that the adjusted data represent residual exotic Zn and Pb. In Figure 4 (d, e), the drill core data and POMP1 plot below the stepping stone data. This is consistent with the average Niton Zn and Pb values of the stepping stones, which are 178 and 67 ppm, respectively, whereas the average Zn and Pb contents of the drill core lavas are 59 and 20 ppm, respectively. Similarly, the Zn and Pb contents of POMP1 are 69.4 and 22.6 ppm, respectively, comparable with the drill cores values and within the ranges quoted in the geological literature for other Vesuvian shoshonites (e.g., Di Renzo *et al*. 2007). Thus, Figure 4 (d, e) shows that the values for Zn and Pb rise above the pristine values of the stepping stone source rock by up to 800 ppm for Zn and 280 ppm for Pb. Therefore, we conclude that the surfaces of the stepping stones are polluted with significant levels of Zn and Pb. It is also apparent that the cleaning process outlined above had not removed all superficial pollution. This suggests that the polluting elements had partly diffused into the rock (Potts *et al*. 2006). The following section will examine the origins of the Zn and Pb pollution, describe their biological effects and attempt to identify variations in the distribution of the pollutants and their possible sources in Pompeii and its hinterland.

DISCUSSION

Pompeii lies within the drainage basin of the Sarno River, which is considered to be the most polluted river in Europe (Cicchella *et al*. 2014). High levels of heavy metal pollution have been recorded in soil samples from the river's hinterland, and Cicchella *et al*. (2014) attribute this pollution to local industrial activity. This includes major activity in agriculture, pharmaceuticals and leather tanning, as well as small and medium-scale activity involving paint manufacture, ceramics and food packaging. Some of the pollutants are at levels high enough to pose a threat to human health. In the Sarno River basin, Zn and Pb pollutants have a similar geographical distribution, occurring in the most urbanized areas where they are both attributed to high vehicular traffic movements: the Zn from dust associated with vehicle tyre wear and the Pb from the use of leaded petrol (Cicchella *et al*. 2014). There are also media reports of major rubbish fires started by the local mafia which involved the burning of tyres.

Origins of Zn pollution

Zn oxide (ZnO) is used in rubber manufacture, which involves a process called vulcanization. This converts natural rubber into a more durable material by heating with sulphur (Heideman *et al*. 2005). This process is activated by the addition of ZnO; a typical car tyre contains about 1.5% ZnO (Wik and Dave 2010). This compound both facilitates the vulcanization process and has a beneficial effect on the physical properties of the rubber (Heideman *et al*. 2005). However, it is known that Zn is an environmental pollutant, so efforts have been made to reduce the amount used in rubber products (Wik and Dave 2009; Ingres-Khans *et al*. 2010). Reduction in the particle size of the ZnO appears to be effective at reducing the quantities required while still maintaining the physical properties of the rubber. For example, some products have reduced particle sizes to 0.02–0.04 μm. This is a considerable reduction when compared with earlier rubbers in which ZnO particle sizes averaged about 0.3–0.4 μm (Heideman *et al*. 2005). In the context of this paper, ZnO particle sizes may be significant in facilitating the dispersion of the ZnO into the environment, particularly by wind. For example, Wik and Dave (2010) noted that $< 5\%$ of the tyre dust is airborne and the concentration of this dust decreases rapidly away from the roads. However, they also noted that the smallest windborne particle sizes (probably < 1 μm) can be transported large distances from the roads.

Footwear production is another important industry requiring significant quantities of vulcanized rubber. For example, the worldwide production of footwear in 2004 was some 17 billion pairs (quoted by Ingres-Khans *et al*. 2010). Ingres-Khans *et al*. (2010) investigated the ecotoxicological effects of leachates from three rubber-soled shoes (shoes 1–3), two from China and one from Vietnam. They filed approximately 1 g from the soles of each pair and leached this material for 29 days in prepared solutions resembling brackish water. These solutions were then filtered and their ecotoxicological effects tested against two common aquatic organisms: a red algae and a crustacean. In each case they recorded growth inhibition and mortality of these organisms. Chemical analyses of the leachates showed that Zn was the most abundant toxic metal. Its concentration varying from 120 μg/L in shoe 1 to 1800 μg/L in shoe 2 and 2500 μg/L in shoe 3. Pb was present in barely trace amounts in the leachates, averaging $<$ 0.2 μg/L. Thus, they concluded that the majority of adverse toxicological effects were related to the concentration of Zn in the leachates (see also Wik and Dave 2010). It is clear, therefore, that rubber from tyre dust and shoe rubber are important potential sources of Zn pollution. For example, Ingres Khans *et al*. (2010) estimate that, on average, each person using one pair of shoes annually will abrade 2 g of particles into the environment. Since the ZnO in these particles is soluble in water, it is possible that this pollutant will enter domestic water supplies via precipitation run-off (Ingres Khans *et al*. 2010).

Origins of Pb pollution

Leaded petrol typically contained around 0.52 g/L Pb in the form of tetraethyl Pb (Nriagu 1990). The toxicity of leaded petrol to human health has been known for many years. For example, it has been estimated that 1.1 million deaths and the loss of 322 million IQ points were attributed annually to Pb pollution from vehicle fuel (quoted in O'Brien 2011). Similarly, a recent study of male infertility in metropolitan Naples (Giaccio *et al*. 2012) established a positive correlation between heavy metal contamination in soils and semen quality. Both Zn and Pb were among the elements implicated in this study. The Pb from burned fuel passes as an aerosol into water, air and food, is deposited on surfaces and soil, and is ingested by humans. Governments have legislated to reduce the Pb content in petrol and in other industrial emissions. Such legislation has produced some very significant results. For example, in the United States, Pb emissions have dropped by 83% since 1990. However, in Italy, implementation of European Commision pollution reduction directives have lagged behind local legislation. For example, Bono *et al*. (1995) monitored incremental reductions in blood and atmospheric Pb levels in Turin in response to successive European Commission directives between 1974 and 1993. When implemented, these directives resulted in very significant reductions in blood and atmospheric Pb levels. Italy finally stopped marketing leaded petrol in January 2002 (Cicchella *et al*. 2014), but as this study demonstrates, environmental Pb pollution persists.

The persistence of Pb pollution on rock surfaces, including archaeological artifacts, is well documented. For example, Worthing *et al*. (2017, 2018) observed the same surface Pb enrichment in an HHpXRF study of second-century paving stones from Trajan's Market in Rome. Comparison between the geochemistry of the lava paving stones and the pristine lavas from which they had been quarried revealed surface enrichment in Pb. This enrichment was attributed to pollution from leaded petrol. Similarly, Potts *et al*. (2006) studied the effects of weathering on the geochemistry of natural outcrops of dolerite and rhyolite from the Preseli Mountains of south Wales. The dolerites are geochemically similar to the paving stones described above. Potts *et al*. cut serial sections of these samples from the surface downwards and, by using an HHpXRF, documented changes in element concentrations with depth. In the dolerites, most element concentrations increased with depth, except for Pb. This element decreased downwards to about 2.5 mm below the surface where the natural lower Pb levels began to be established. They attributed this pattern to superficial surface enrichment of Pb because of 'automobile exhaust emissions' in which Pb has diffused into the surface layers of the rock. It is interesting to note that this pollution occurs on rock outcrops that are in excess of 1 km from the A278 main road and lie in a sparsely populated area. It is also significant that the UK stopped marketing leaded petrol in 2000. Thus, the apparent longevity of the Pb pollution in both natural rocks and archaeological artifacts may be explained by the diffusion of the Pb into the surface layers of the materials. This appears to render at least some of the Pb inaccessible to the thorough cleaning that preceded the present Niton analyses.

Atmospheric dispersion of Zn and Pb

A considerable amount of research on the origin and atmospheric dispersion of anthropogenic pollutants has largely been driven by concerns about human health (e.g., Harrison and Yin 2000; AQEG 2005; Vallero 2008). These substances are transported as mixtures of particles of different sizes and are known collectively as atmospheric particulate matter (PM) or aerosols. As well as particle size, dispersion is controlled by meteorological factors such as temperature, humidity and wind speed. Aerosols are suspensions of solid or liquid particles in air that may include a fluid phase such as water. They are classified according to their size. The upper limit is PM_{10}, which represents particles ≤ 10 µm in diameter but > 2.5 µm. They are classified as coarse PM. $PM_{2.5}$ are particles ≤ 2.5 µm and are classified as fine PM. The latter include carbon combustion particles, organic compounds, dust and trace metals such as Zn and Pb. Their small size renders them capable of penetration into the deeper areas of human lungs and they are therefore potentially the most toxic. Harrison and Yin (2000) have shown that both coarse and fine PM were detected at roadside monitoring stations in several cities in the United States, Europe and Pakistan. Their significance in the context of this paper is that they are also capable of dispersion in the atmosphere over large distances (AQEG 2005).

The evidence presented above suggests that $PM_{2.5}$ containing Zn may include some dust from abraded vehicle tyres together with the products of tyre burning. This implies that Zn pollution on the stepping stones may be a combination of atmospheric Zn-bearing PM plus Zn from direct contact between rubber-soled shoes and vehicle tyres. The Pb pollution is derived from the burning of leaded petrol from on-site vehicles, possibly supplemented by Pb-bearing PM emissions from source roads outside Pompeii. The following section will assess the relative importance of these different sources and how they have contributed to the distribution of pollution across the city.

DISTRIBUTION OF ZN AND PB POLLUTANTS IN POMPEII

In order to assess distribution of the two pollutants, the location of each stepping stone was accurately georeferenced (Poehler 2017b); the relative concentrations of Zn and Pb are represented by the diameter of the circles in Figure 5 (a, b). On the scale of these diagrams, each individual stepping stone could not be represented (Fig. 1), thus the circular symbols for each stone tend to overlap. However, where there is overlap, the diameter of the symbols represents the highest value of the individual stones under each symbol, not a cumulative total of these stones.

Zinc

We have suggested above that tourist footfall may be a significant cause of the observed Zn pollution on the stepping stones. However, we have also concluded that the distribution of pollution is influenced not only by the magnitude of inputs from the different possible sources but, also, by the ways in which tourists access the site. This implies that tourist footfall across the site and tourist use of the stepping stones may not be directly related. For example, most visitors enter through Porta Marina either as individuals or in guided groups. At this early stage of their visit, they are intent on getting into the site and thus tend to follow a linear uphill route towards the Forum along Via Marina. This will involve walking either along the pavement or the road, but not the stepping stones which in this area are the lowest in height in the city and thus easily missed. Additionally, for those visitors who wish to cross Via Marina, they can do so at any point along the street, without pressure to use the stepping stones. This is unlike many other locations in the city, such as at street intersections (Fig. 1), where the visitor would need to go out of their way not to use the stepping stones to cross the street. This explains the lower Zn pollution levels observed along Via Marina, a well-frequented route by tourists. However, once at the top of the slope, tourist behaviour tends to switch from linear to lateral movement. They fan out, either moving towards the Temple of Apollo to the left of the street or to the Basilica on the right or straight ahead to the Forum and then onwards into the rest of the site. The higher levels of Zn pollution occur in situations where tourists are not necessarily seeking destinations such as the

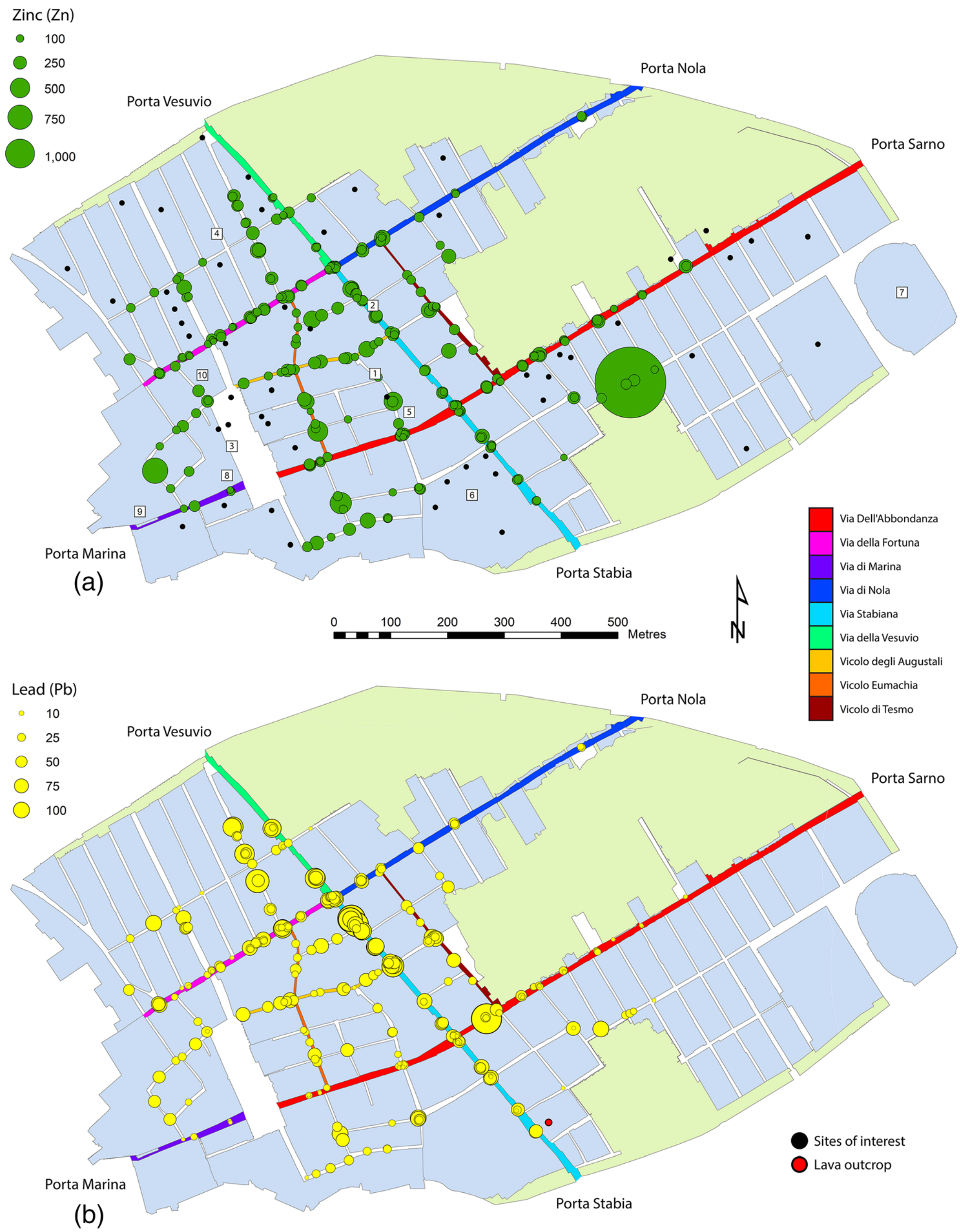

Figure 5 *(a) Distribution of Zn pollution in Pompeii. Localities mentioned in the text are numbered in boxes as follows: 1, Brothel; 2, Casa di Marcus Lucretius; 3, Forum; 4, House of Vettii; 5, Stabian Baths; 6, theatres; 7, Amphitheatre; 8, Temple of Apollo; 9, Basilica; and 10, Central Baths. (b) Distribution of Pb pollution in Pompeii. Streets mentioned in text are colour coded and all concentrations are in ppm. [Colour figure can be viewed at wileyonlinelibrary.com]*

House of the Vettii, but are acting in an exploratory mode, walking at a slower pace that allows for the crossing of streets using the stepping stones (Fig. 1). It is in crossing the streets that tourist footfall creates the observed pattern of pollution. This effect will be amplified where very large groups are involved. Thus, the movement pattern associated with stepping stone use is one that involves looking at houses, shops and so on on both sides of the street or at intersections where tourists are required to cross the intervening street (Fig. 1).

Figure 5 (a) shows the distribution of Zn pollution on stepping stones across the site together with the distribution of the main archaeological destinations for tourists. One striking feature is that Zn pollution is not uniformly present, even though we measured stepping stones over the whole area open to the public. It is most strongly developed in areas visited by tourists probably in the exploratory mode described above. This suggests that atmospheric PM was not responsible for the observed patterns. Had this been the case, a more even distribution of the pollution might have been expected. The highest concentrations tend to occur in the areas west of Via Stabiana and Via del Vesuvio (Fig. 5, a), where many of the important archaeological places of interest are located. However, there are also some significant concentrations immediately to the east of Via Stabiana. The lowest concentrations are found at the ends of *vie* Stabiana, del Vesuvio, dell'Abbondanza and Nola, that is, on the margins of the city and furthest from the main entrance for tourists at Porta Marina. The higher Zn concentrations to the east of the Forum, particularly in Vicolo degli Augustali, may also define a tourist route that leads to such sites as the brothel, which has a small spike in Zn outside it, and onwards to the Stabian Baths and theatres. There is also a significant east to west concentration along Via dell'Abbondanza to the east of Via Stabiana. This route leads to the Amphitheatre via other sites along the way. These associations clearly suggest a positive correlation between tourist footfall and Zn concentrations.

Notwithstanding the above comments, the picture may be more complex. For example, there are significant Zn concentrations associated with streets in the central region around the Forum, which for many years were closed to the public: Vicolo di Eumachia east of the Forum and Vicolo di Tesmo (Fig. 5, a) east of Via Stabiana. Footfall in these closed streets may be associated with staff at Pompeii using the closed streets to traverse the site. We also need to consider the passage of the rubber tyred service vehicles, which in some cases may have resulted in significant pollution. For example, the highest reading for Zn was found at the access point to the vehicle parking lot situated in the south-east of the city. This suggests that the stepping stones may also carry a Zn signature from such vehicles. Indeed, Figure 6 shows the clear imprint of rubber tyre treads on stepping stones along Via Stabiana. However, we did not observe any comparable examples during the fieldwork. This may be partly explained by the former presence of wooden ramps over the stepping stones on Via Stabiana, which is obviously a major access conduit within the site. These ramps allowed the passage of large mini-dump truck vehicles carrying construction materials and would have protected the sides of the stepping stones from contact with vehicle tyres, though the top would have sustained contact. We may conclude, therefore, that it is unclear to what extent vehicle tyres will have left a Zn signature on the stepping stones. We also cannot assess the effects of wind-borne PM aerosols on Zn pollution, but if this were substantial we would have expected the Zn signature to be more widespread because of the blanketing effect of such airfall pollution.

In conclusion, we suggest that tourist footfall provides the most coherent evidence-based explanation of the patterns observed. The overall effects of abraded tyre and wind-borne Zn-bearing PM cannot be assessed.

Lead

The distribution of Pb pollution is shown in Figure 5 (b). The stepping stones associated with higher levels of Pb pollution tend to be in those streets most accessible to vehicles. The section

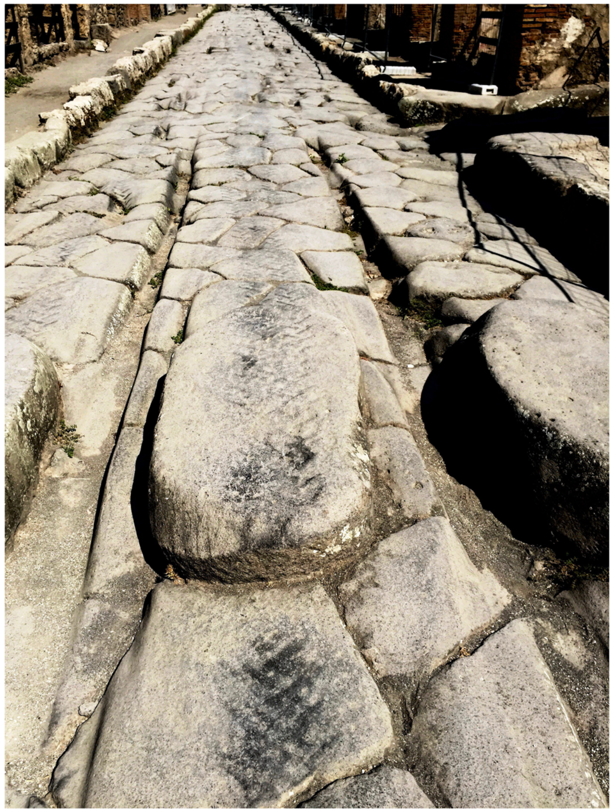

Figure 6 *Vehicle tyre marks across stepping stones near the Casa di Marcus Lucretius on Via Stabiana. Photo: courtesy of Sophie Hay. [Colour figure can be viewed at wileyonlinelibrary.com]*

of Via dell'Abbondanza between the Forum and the junction with Via Stabiana and also in Via Marina shows the lowest levels of Pb pollution. These street sections are difficult for vehicles to access because they are associated with high tourist footfall, and there are clear impediments, including the differential in street height at the junction of Via dell'Abbondanza and Via Stabiana. A combination of the gradient and presence of a very rutted ancient road surface in Via Stabiana may have caused a higher level of Pb pollution because of the difficulties of navigation where the street slopes and has a heavily rutted surface and many crossing stones to negotiate. This is probably a challenge to drivers of vehicles and may explain the higher levels of Pb pollution. The overall pattern diverges from that found for Zn, particularly in the streets to the east and west of the Forum that have for long periods of time been closed to the public. Simply put, the preferred access route for vehicles would seem to be a north–south access based on Via Stabiana from which other parts of the site could be accessed, particularly using Via della Fortuna and Vicolo degli Augustali. The contrast between Zn and Pb associated with the access point for vehicles from the unexcavated section to the south of the site may point to a lower incidence of the use of vehicles on-site before 2002, when leaded petrol ceased to be available in Italy. It is also possible that the incidence of the use of vehicles and, perhaps, the size of vehicles on the site has increased with the advent of the major restoration project, Grande Progetto Pompei, from 2012 to the present. However, evidence presented above suggests that the Pb can also be dispersed as a pervasive aerosol perhaps over considerable distances. Thus, it is also possible that some of the Pb pollution may be derived from traffic in the modern town that surrounds the site and from the nearby E45 motorway. However, if this were the case, it would be expected that Pb pollution would be more in evidence across the whole site. In fact, there are many areas where there is almost no Pb pollution at all. This implies that that the most important source was from on-site vehicles.

SUMMARY AND CONCLUSIONS

An HHpXRF study of stepping stones and drill core material from ancient Pompeii revealed that surface concentrations of Zn and Pb were considerably higher on the stepping stones than in the drill cores material which had been shielded from atmospheric pollution. It was concluded that the surface enrichment in Zn was derived from the abrasion of rubber-soled shoes worn by the very large number of tourists who visit the site every year, and to a lesser extent from tyre abrasion and PM from the burning of tyres. The Pb pollution was attributed to recent emissions from leaded petrol and is most abundant in streets that have been accessible to site vehicle traffic. It was suggested that the apparent environmental persistence of Pb was caused by diffusion of the element into the surface layers of the stepping stones.

The serious ecotoxicological effects of Zn and Pb pollution were also noted above (e.g., Wik and Dave 2009; Ingres-Khans *et al.* 2010; O'Brien 2011). At Pompeii, movement of these pollutants is most likely to occur in the autumn and winter when rainfall peaks (Oct-Feb over 100mm per month), thus maximizing run-off. During this period pollutants will be washed into water courses and out to sea where the potential for toxic effects on marine organisms is high. The Bay of Naples is particularly popular for its seafood. There is also the possibility of these pollutants entering the public water systems. However, there are already high levels of heavy metal pollution associated with modern industrial activity in the Sarno River basin (Cicchella *et al.* 2014). It is thus unlikely that the input of Zn and Pb from Pompeii will add significantly to the pollution load already entering the environment. However, it is worth noting that there are many historical and archaeological sites around the world visited by very large numbers of people. Given the ubiquity of Zn-bearing tyre dust and rubber-soled shoes, it is suggested that local authorities should be aware of possible Zn pollution hotspots and the associated risks of this toxic element entering the local environment. Similar arguments apply to urban areas with high human populations and traffic densities.

ACKNOWLEDGEMENTS

The authors thank Professor Massimo Osanna at the Soprintendenza di Pompei, Ercolano e Stabia for permission to conduct the survey, as well as the custodians of the site for access to the sample locations. They also thank Dr Giovanni Di Maio, who provided a sample of the drill core for inductively coupled mass spectrometry (ICP-MS) analysis and assisted with locating the borehole site. Dr Sophie Hay kindly provided the photograph used in Figure 6. The authors are also grateful to Professor Dave Wray of the University of Greenwich, London, who kindly performed the ICP-MS analysis, read a draft of the paper and made useful suggestions. They also thank the University of Kent, Canterbury, for loaning the Niton X-ray analyser (XRF) used in the project. Finally, they thank Dr Fabrizio Marra and an anonymous referee for helpful reviews of an earlier version of this paper.

REFERENCES

AQEG, 2005, *Particulate matter in the UK: Summary*, Defra, London.

Bono, R., Pignata, C., Scursatone, E., Rovere, R., Natale, P., and Gilli, G., 1995, Updating about reductions of air and blood concentrations in Turin, Italy, following reductions in the Lead content of gasoline, *Environmental Research*, **70**, 30–4.

Cicchella, D., Giaccio, L., Lima, A., Albanese, S., Cosenza, A., Civitello, D., and De Vivo, B., 2014, Assessment of the topsoil heavy metals pollution in the Sarno River basin, South Italy, *Environmental Earth Sciences*, **71**, 5129–43.

Di Renzo, V., Di Vito, M. A., Arienzo, I., Carandente, A., Civetta, L., D'Antonio, M., Giordano, E., Orsi, G., and Tonarini, S., 2007, Magmatic history of Monte Somma-Vesuvius on the basis of new geochemical and isotopic data from a deep borehole (Camaldoni della Torre), *Journal of Petrology*, **48**, 753–84.

Giaccio, L., Cichella, D., De Vivo, B., Lombardi, G., and De Rosa, M., 2012, Does heavy metal pollution affects semen quality in men? A case of study in the metropolitan area of Naples (Italy), *Journal of Geochemical Exploration*, **112**, 218–25.

Harrison, R. M., and Yin, J., 2000, Particulate matter in the atmosphere: Which particle properties are important for its effects on health? *The Science of the Total Environment*, **249**, 85–101.

Heideman, G., Datta, R. N., Nordermeer, J. M. W., and Van Baarle, B., 2005, Influence of zinc oxide during different stages of Sulphur vulcanization, Elucidated by model compound studies.. *Journal of Applied Polymer Science*, **95**, 1388–404.

Ingres-Khans, E., Ruden, C., and Breitholtz, M., 2010, Chemical risks and consumer products: The toxicity of shoe soles, *Ecotoxicology and Environmental Safety*, **73**, 1633–40.

Kastenmeier, P., Di Maio, G., Balassone, G., Boni, M., Joachimski, M., and Mondillo, N., 2010, The source of stone building materials from the Pompeii archaeological area and its surroundings, *Periodico di Mineralogia Special Issue*, 39–58.

Nriagu, J. O., 1990, The rise and fall of leaded gasoline, *The Science of the Total Environment*, **92**, 13–28. http://www.attalus.org/info/pliny.html

O'Brien, E. 2011. Chronology of leaded gasoline/leaded petrol history. The Lead group Inc. 1–20.

Pliny the Younger *Letters*, 6.16 and 6.20.

Poehler, E. E., 2017a, *The traffic Systems of Pompeii*, 276, Oxford University Press.

Poehler, E.E. 2017b. The Pompeii bibliography and mapping project. https://digitalhumanities.umass.edu.

Potts, P. J., Bernardini, F., Jones, M. C., Williams-Thorpe, O., and Webb, P. C., 2006, Effects of weathering on in-situ portable X-ray fluorescence analyses of geological outcrops: Dolerite and rhyolite outcrops from the Preseli Mountains, South Wales, *X-Ray Spectroscopy*, **35**, 8–18.

Russel, B. 2013. Gazeteer of stone quarries in the Roman world. Version 1.0. Oxford Roman economy project. www.romaneconomy.ox.ac.uk.

Sigurdsson, H., Cashdollar, S., and Sparks, S. R. J., 1982, The eruption of Vesuvius in AD 79: Reconstruction from historical and Volcanological evidence, *American Journal of Archaeology*, **86**, 39–51.

Vallero, D. A., 2008, *Fundamentals of air pollution*, 942, Elsevier Inc.

Wik, A., and Dave, G., 2009, Occurrence and effects of tire wear particles in the environment – A critical review and an initial risk assessment, *Environmental Pollution*, **157**, 1–1.

Worthing, M., Browning, J., Laurence, R., and Bosworth, L., 2017, Geochemical methods for sourcing lava paving stones from the Roman roads of Central Italy, *Archaeometry*, **59**, 1000–17.

Worthing, M., Laurence, R., and Bosworth, L., 2018, Trajan's forum (hemicycle) and via Biberatica (Trajan's market): An HHpXRF study of the provenance of lava paving in ancient Rome (Italy), *Archaeometry*, **60**, 1202–20.